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A method of tracing the temperature and oxygen-fugacity histories of complex magnetite–ilmenite grains

JOHN F. W. BOWLES[1]

Department of Geology, University College, London EC1E 6BT

SUMMARY. The formation of ilmenite from titanomagnetite frequently shows separate generations of production. The ilmenite products can be combined with the magnetite host to represent the intermediate stages in this development. Use of the Buddington and Lindsley (1964) geothermometer in conjunction with this method provides a number of points in the temperature and oxygen-fugacity history of a single, complex magnetite–ilmenite grain.

Application of the method is illustrated by an example from the Freetown layered gabbro. A titanomagnetite exsolved granular ilmenite whilst cooling and this process ceased at 930°C and an oxygen fugacity of $\log f_{O_2} = -11{\cdot}5$. Further cooling and exsolution continued until the grain reached 662 °C and $\log f_{O_2} = -19{\cdot}0$, producing distinct ilmenite lamellae.

MANY authors have described magnetite–ilmenite associations that indicate several generations of ilmenite formation. Edwards (1938), Evrard (1949), Vincent (1960), and Siemiatkowski (1970) have described textures that they consider indicate an origin of the various generations of ilmenite by exsolution from an original titaniferous magnetite. Buddington *et al.* (1955) and Heier (1956) took the view that the ilmenite adopted various different morphologies during crystallization. Wright (1961) provided evidence in support of the exsolution hypothesis and Buddington and Lindsley (1964) suggested a mechanism of oxidation followed or accompanied by exsolution. Anderson (1968, p. 537) recorded similar compositions and oxygen isotope ratios for lamellar ilmenite and granular ilmenite in a specimen from the La Blanche Lake titaniferous magnetite deposit in Quebec.

Two generations of ilmenite in specimen BA 879 (analysed here and described by Wells, 1962, pp. 102–4), from the Freetown layered gabbro, also have similar compositions, and Elsdon (1972, p. 949) notes the same association in gabbros from Kap Edvard Holm, East Greenland.

Anderson concluded that the uniformity of composition is due to equilibration by cation exchange between the two phases of ilmenite and the magnetite, but the textural evidence does not in general appear to be consistent with this conclusion.

The textural relationship of BA 879 is shown in fig. 1, where it is seen that there are three generations of ilmenite.

The first generation of ilmenite is homogeneous, with minor hematite lamellae, while the second generation of ilmenite produces coarse {111} lamellae and the third generation of ilmenite, which forms very fine {111} lamellae, occurs between the lamellae of the second generation, but does not approach them closely. This generation of ilmenite is only visible under high power with oil immersion and is found in areas also occupied by {100} ceylonite lamellae.

It is likely that cation mobility decreased as cooling proceeded: segregation of granular ilmenite occurred at high temperature, which permitted the cations to move relatively freely

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[1] Present address: Institute of Geological Sciences, 64–78 Gray's Inn Road, London WC1X 8NG.

within the magnetite. Later, when the coarse ilmenite lamellae were formed, the cations were less mobile and the evenly distributed coarse lamellae gathered titanium from their own 'catchment' areas. Similarly, the third stage of fine lamellae was produced when the cation mobility was further reduced by falling temperature.

Similar series of events are described by Buddington and Lindsley (1964, p. 323) and by Siemiatkowski (1970).

This textural interpretation conflicts with Anderson's conclusion, and it becomes necessary to ask two questions. If cation mobility cannot explain the similarity of composition of two phases of ilmenite, what other mechanism can give rise to this similarity? Secondly, if cooling is a continuous process, why is the ilmenite produced in several distinct episodes and why is there not a continuous gradation in size from ilmenite grains to fine lamellae? A possible answer to this second question is to argue that cooling is not continuous, but there is no evidence from other minerals in specimen BA 879 to suggest that this is a possibility and examples of several generations of ilmenite have been widely reported from elsewhere, so it is not realistic to invoke special circumstances. The mechanism of ilmenite production is not understood, but it is not impossible that there is a threshold degree of oxidation, which must be exceeded if the mechanism is to proceed. The cooling path followed by a normal magma in the temperature and oxygen-fugacity field shows an extremely rapid decrease in oxygen fugacity for a small fall in temperature. The oxygen must either escape from the system or be taken up by the iron-oxide phases. Continuous cooling thus implies a continuous oxidizing influence, which will be expressed by the formation of ilmenite in distinct generations if an oxidation threshold is to be exceeded before the ilmenite can be produced.

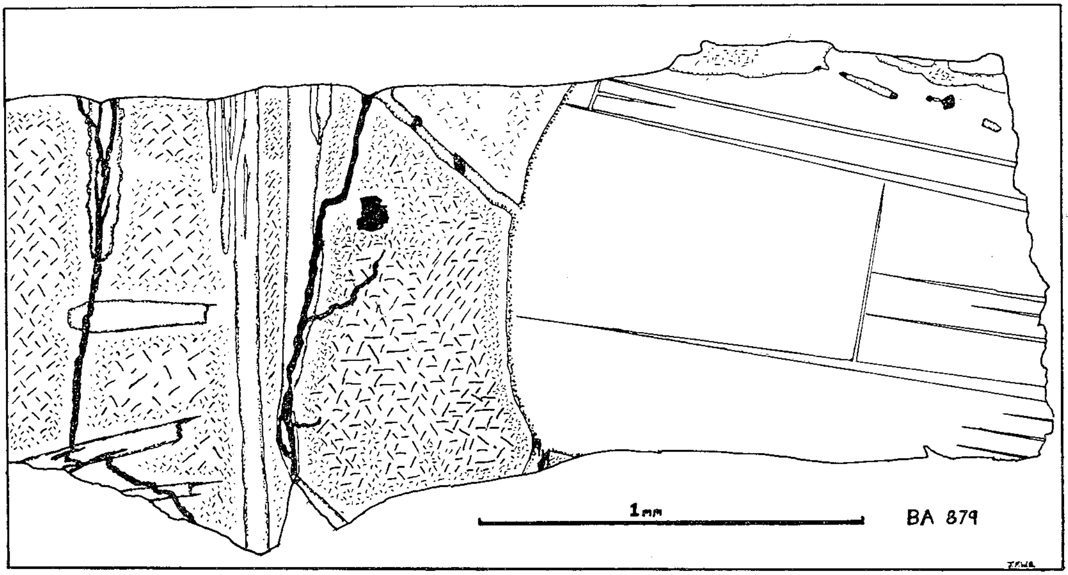

FIG. 1. Ilmenite–magnetite grain (specimen BA 879) from the Freetown layered gabbro. The granular ilmenite (right) is homogeneous except at the margins and contains tapering hematite lamellae. The magnetite (left) contains broad {111} ilmenite lamellae, which, like the granular ilmenite, show a reaction rim containing blades of a Mn spinel (?). The magnetite contains {100} ceylonite lamellae, which become smaller towards the margins of the magnetite and are absent from a zone adjacent to those margins. Superimposed on the network of ceylonite lamellae is a network of fine {111} ilmenite lamellae (not shown).

It must also be noted that the ilmenite–hematite contours of the Buddington and Lindsley geothermometer do not diverge very much from the buffer lines. Several authors (e.g. Anderson, Buddington, Dasgupta, and Czamanske—see note by Czamanske and Mihálak, 1972, p. 507), accept the idea that the cooling curve of a magma in the oxygen-fugacity and temperature field normally parallels the buffer lines. Thus with cooling, various generations of ilmenite in the same specimen are likely to have similar compositions and it is the composition of the magnetite that shows the greatest change.

Two generations of ilmenite production. Consider the common example of a rock containing both early ilmenite grains and magnetites with later ilmenite lamellae. Application of the data of Buddington and Lindsley to the compositions of the magnetite and its ilmenite lamellae gives a point in the temperature and oxygen-fugacity history of the grain corresponding to the time when Ti ceased to be mobile over short distances within the magnetite. If it were possible to estimate the composition of the magnetite before the ilmenite lamellae were produced, then it would be possible to use this composition, with the composition of the separate ilmenite grain, to determine the temperature and oxygen fugacity corresponding to the time when Ti was no longer able to enter or leave individual grains. The mechanism of production of ilmenite lamellae in magnetite is not totally understood (Buddington and Lindsley, 1964, pp. 318–22), but for the present argument this is not important, since we are concerned only with the final result, which is the same whatever the process.

Oxidation processes will take place along the $Ti/(Ti+Fe)$ contour (fig. 2), whereas processes involving a loss or gain of Ti will occur along lines radiating from the Ti apex, which are lines that show no change in the ratio of Fe^{2+} to Fe^{3+}. Whether the processes occur separately or together, they may be resolved into these two directions. A probable sequence is outlined in fig. 2, where an initial titanomagnetite of composition A is divided into an ilmenite (B) and a less titaniferous magnetite (C). Late stage oxidation of these phases will give final compositions such as D and E. When the magnetite and the ilmenite lamellae are analysed in the microprobe and the results reduced along the $Ti/(Ti+Fe)$ contour to the appropriate solid–solution series, the analyses will give the composition B for the lamellae and C for the host. The relative volumes of the two phases may be estimated from a measurement of the areas of the two phases. The composition A′ can then be calculated using the ratio of volumes and knowledge of the volumes of the various unit cells. The composition A′ can be reduced, at constant $Ti/(Ti+Fe)$, to give the original composition A.

Multi-generation ilmenite production. It should be possible to apply this technique repetitively to several generations of ilmenite production and obtain a series of points in the temperature and oxygen-fugacity history of a particular grain. Although there are three phases of ilmenite production in the specimen described, the latest phase was too small for microprobe analysis and this extension of the technique is not attempted here.

Since the third generation of ilmenite in specimen BA 879 is extremely fine grained and only 2 or 3 examples of this generation can be found in the entire section, it is not considered that the ensuing calculations will be adversely affected by neglecting this generation of ilmenite.

Calculations on a single specimen from the Freetown layered gabbro. This specimen, BA 879, illustrated by fig. 1, is represented in these calculations as a magnetite, a lamellar ilmenite, and a granular ilmenite. The compositions of these phases are given in Table I, which includes the results of the minor-element calculations for the magnetite and ilmenite.

The analyses were obtained using an early CAMECA microprobe modernized by the author. Pure metal standards were used for elements of atomic number 22 and over, whilst silicate standards, kindly provided by Dr. A. M. Clark, were used for the lighter elements. The computer programme devised by Mason *et al.* (1969) provided the necessary correction procedure, and the data were prepared for this programme using the techniques described in Bowles (1976). Several methods have been proposed for recalculating titanomagnetite and ilmenite analyses to take account of the minor elements. Some of these methods incorporate the minor elements in the final result (Vincent *et al.*, 1957, and Carmichael, 1967) whilst other methods (Wones in Buddington and Lindsley, 1964, and Anderson, 1968) discard the minor elements to produce a result involving only the pure Fe–Ti–O system. The method adopted here is that due to Wones as modified by Anderson. It has been found (Bowles, in preparation) that the temperature and oxygen fugacity obtained from the use of the Buddington and Lindsley geothermometer can vary considerably depending upon the recalculation procedure used. Comparisons between the results of various authors can be misleading unless the same method of calculation is used.

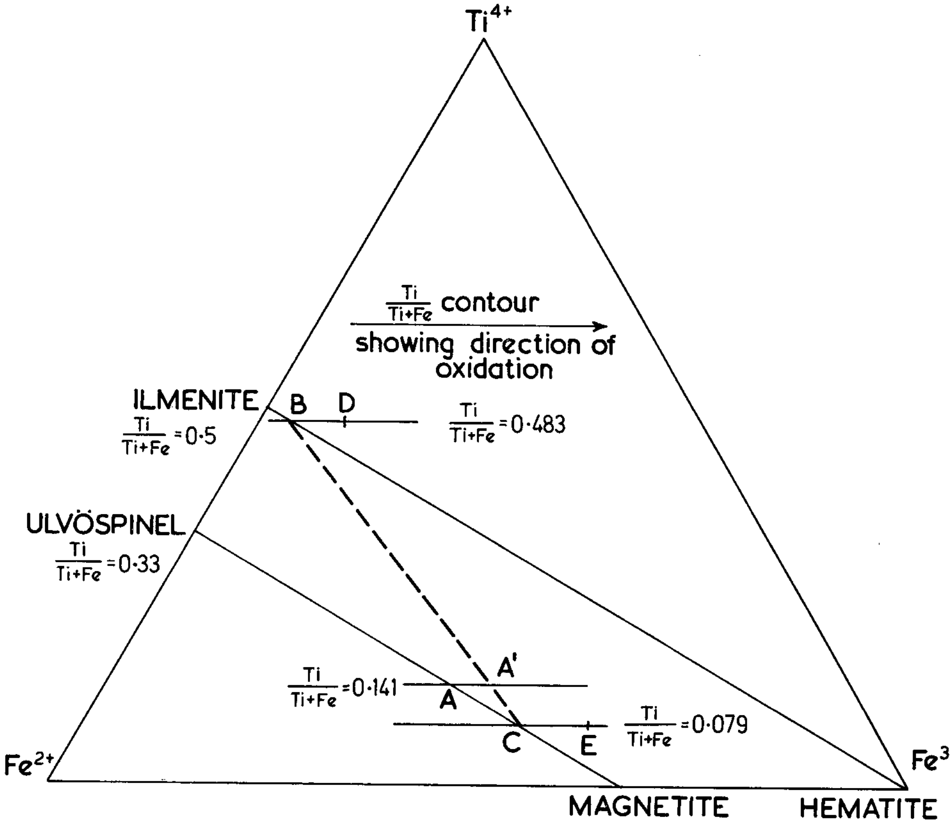

FIG. 2. The TiO_2–FeO–Fe_2O_3 system plotted in terms of metal ions to show the Ti/(Ti+Fe) contours, and oxidation and exsolution process in relation to the magnetite–ulvöspinel and ilmenite–hematite solid solution series. Drawn by C. Stuart.

An allowance for the hematite lamellae, based on point counting, has been added to the composition of the granular ilmenite and the same correction applied. This results in a composition of ilmenite 88·0 %, hematite 12·0 %.

Point counting, over an area of the specimen larger than fig. 1, and including a large number of similar magnetite–ilmenite grains in various orientations, showed that the lamellae ilmenite occupies 16·1 % of the area of the magnetite and lamellar ilmenite taken together. The magnetite host contains 23·7 % ulvöspinel and is represented on fig. 2 by a Ti/(Ti+Fe) ratio of 0·079 whilst the ilmenite lamellae contain 3·4 % hematite and are represented by a Ti/(Ti+Fe) ratio of 0·483. An average 1 cm^3 of the intergrowth contains 0·161 cm^3 of ilmenite and 0·839 cm^3 of magnetite. The unit-cell volume of the titanomagnetite containing 23·7 % ulvöspinel can be calculated from the unit cell dimensions of pure magnetite ($a = 8{\cdot}396$ Å) and pure ulvöspinel ($a = 8{\cdot}53$ Å). This volume is $5{\cdot}986 \times 10^{-22}$ cm^3. Similarly the unit cell volume of the ilmenite ($a_{\text{hex}} = 5{\cdot}089$ Å, $c_{\text{hex}} = 14{\cdot}163$ Å) containing 3·4 % hematite ($a_{\text{hex}} = 5{\cdot}035$ Å, $c_{\text{hex}} = 13{\cdot}749$ Å) is $3{\cdot}171 \times 10^{-22}$ cm^3. Hence 0·161 cm^3 of the ilmenite lamellae contain $0{\cdot}51 \times 10^{21}$ unit cells which represent $6{\cdot}12 \times 10^{21}$ atoms of Fe and Ti taken together on the basis of 6 (Fe, Ti)$_2$O$_3$ atoms within the ilmenite hexagonal unit cell. Similarly 0·839 cm^3 of the magnetite contains $1{\cdot}40 \times 10^{21}$ unit cells representing $33{\cdot}6 \times 10^{21}$ atoms of Fe+Ti on the basis of a magnetite unit cell containing 8 (Fe, Ti)$_3$O$_4$ atoms. Of the atoms in the magnetite 0·079 are Ti as are 0·483 of the atoms in the ilmenite. Thus the total number of Fe+Ti atoms in an average 1 cm^3 of the intergrowth is $39{\cdot}72 \times 10^{21}$ of which $5{\cdot}61 \times 10^{21}$ are Ti atoms. This represents a Ti/(Ti+Fe) ratio of 0·141 and is indicated as a line on fig. 2, passing through the composition A′. If the intergrowth is homogenized and reduced to the ulvöspinel–magnetite solid-solution series along the Ti/(Ti+Fe) contour, a titanomagnetite (A) is obtained that contains 42·3 % of the ulvöspinel end-member.

TABLE I. *Composition of the principal phases of fig. 1*

	FeO	Fe$_2$O$_3$	TiO$_2$	Al$_2$O$_3$	Cr$_2$O$_3$	V$_2$O$_3$	MnO	MgO	SiO$_2$	Total
Magnetite	34·32	45·19	8·07	5·05	0·85	1·09	0·21	3·00	0·24	98·02*
Lamellar ilmenite	38·47	3·02	52·35	0·62	0·04	0·35	0·70	4·56	0·21	100·32
Granular ilmenite	39·57	2·65	52·27	0·49	0·11	0·29	0·53	3·92	0·08	99·91

	Molecular proportions†					Molecular percentages‡	
	2*R*O.SiO$_2$	(*R*$_{0·7}$Fe$_{0·3}$)O.*M*$_2$O$_3$	2*R*O.TiO$_2$	2FeO.TiO$_2$	Fe$_3$O$_4$	Ulvöspinel	Magnetite
Magnetite	0·0039	0·0623	0·0130	0·0881	0·2830	23·7	76·3
Ilmenite:	*R*O.SiO$_2$	*M*$_2$O$_3$	*R*O.TiO$_2$	FeO.TiO$_2$	Fe$_2$O$_3$	Ilmenite	Hematite
lamellar	0·0036	0·0088	0·1194	0·5355	0·0189	96·6	3·4
granular	0·0013	0·0074	0·1034	0·5508	0·0167	88·0§	12·0§

* This figure corresponds to magnetite computed to lie on the solid-solution series. Late oxidation will have increased Fe$_2$O$_3$ at the expense of FeO, leading to an increase in the total.

† R = Mn+Mg; M = Al+Cr+V.

‡ Major phases normalized to 100 %.

§ Including 9·4 vol. % = 10·4 wt. % hematite lamellae.

This composition together with the composition of the granular ilmenite may be applied to the temperature and oxygen-fugacity curves of Buddington and Lindsley (1964) to give a temperature of 930 °C and an oxygen fugacity of $\log f_{O_2} = -11{\cdot}5$. Similarly the compositions obtained for the magnetite and the ilmenite lamellae give a temperature of 660 °C and oxygen fugacity of $\log f_{O_2} = -19{\cdot}0$. The method by which these results are produced from the data of Buddington and Lindsley are given in detail by Bowles (1976). If the two temperature and oxygen-fugacity results obtained here are placed with the buffer reactions from Verhoogen (1962) on a graph of temperature against oxygen fugacity, then a line drawn between the two results roughly parallels the buffer reactions; this exercise is conducted by Bowles (1976). Reference has already been made to the suggestion that cooling curves in the temperature and oxygen-fugacity field probably parallel the buffer reactions, so the parallelism achieved by the present results suggests that these results are realistic.

The only experimental work on iron–titanium oxides from other layered gabbros has been performed under unknown oxygen fugacity conditions. However, the varying cation mobility that gives rise to the several generations of ilmenite is dependent only on temperature, so that the experimental work can be used as a check on the results obtained here.

It has been shown by Vincent *et al.* (1957) that ilmenite lamellae from Skaergaard, corresponding to the second generation ilmenite described here, formed between 600 and 750 °C, so that with slow crystallization the equilibration temperature of 660 °C obtained here seems reasonable.

Work described by Wright (1959), on the same Skaergaard samples, showed that homogenization of magnetite–ilmenite intergrowths could be achieved by heating, under reducing conditions, to between 940 and 1250 °C. Other evidence from Freetown (Wells, 1962) indicates that the crystallization of the pyroxenes in the gabbro occurred at approximately 1070 °C. The oxides in the pegmatitic segregation represented by specimen BA 879 crystallized below this temperature, and equilibration of the granular ilmenite and magnetite at 930 °C, as suggested here, would thus appear to be realistic. The equilibration temperature of 930 °C should be reliable whether the granular ilmenite was produced from the titaniferous magnetite or crystallized independently. The conditions of 930 °C and $\log f_{O_2} = -11{\cdot}5$ have been deduced on the assumption that the granular ilmenite reached equilibrium with an original titaniferous magnetite and that the exsolution of the later lamellar ilmenite can be 'reversed' by the calculations used here. The realistic nature of the result in terms of temperature and position relative to the buffer reactions provides indirect evidence that these assumptions may have some validity.

Estimation of errors

A discussion of the probable errors of the present procedure and of the comparative errors introduced by using different methods of treatment of the minor elements will appear as an Appendix in the Miniprint section of a later 1977 issue.

Conclusion. It is concluded that the separation of granular ilmenite from magnetite in specimen BA 879 from the Freetown layered gabbro ended at 930 ± 3 °C, $\log f_{O_2} = -11{\cdot}5 \pm 0{\cdot}1$ and that continued cooling produced lamella ilmenite, which equilibrated at 660 ± 1 °C, $\log f_{O_2} = -19{\cdot}0 \pm 0{\cdot}2$.

These figures indicate the extended subsolidus equilibration processes that occur in iron–titanium oxides and the presence of the third generation of ilmenite shows that the process continued below 660 °C. The results given here should not be compared with temperature and oxygen-fugacity determinations other than those calculated according to the Wones–Anderson method and, since the Freetown iron–titanium oxides are particularly rich in impurities, caution should be exercised when making comparisons with other intrusions.

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